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STUDIES ON PAPER PULPS

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I. INTRODUCTION

Paper making, as a mechanical art, is governed by the physical characteristics of the fiber in the material used for its production. These characteristics are chiefly the length, strength, color, bulk, and degree of softness of the fibers. It is generally recognized that the various pulps used in the manufacture of paper contain residues of lignin and resins not wholly removed in the preparation of the pulp or in the subsequent bleaching. This is particularly true of the celluloses of the woods in which the lignin and

other noncellulose materials are removed by either acid or alkaline processes. The woods are treated long enough to remove the incrusting materials without damaging the residual cellulose. The fiber characteristics are further modified by the subsequent bleaching, sizing, and beating. Consequently, the pulps have an individuality which is manifested in their behavior toward certain chemical reagents.

Much work has already been done, both with the woods from which the pulps are produced and with the pulps themselves, in studying these properties of the fibers and in seeking to find means of judging the paper-making value by laboratory tests in advance. The results are scattered over a wide range of chemical literature, and for the most part are concerned with pulps produced in other countries. The present work has been carried out chiefly with typical American pulps produced by the several well-known methods, in order to ascertain their chemical characteristics as far as possible with the few reliable quantitative methods available.

On the assumption that the disintegration of paper pulp is a result of conditions causing oxidation and hydrolysis, the susceptibility of pulps to chemical reagents producing such changes ought to be shown to some extent by their loss in weight. The pulps therefore have been subjected to the action of oxidizing and hydrolyzing reagents and the loss in weight determined. .

II. PULPS USED

The samples employed consisted of cooked, bleached, and thoroughly washed rags in the form of "half-stuff" prepared from new stock, sulphite spruce bleached and unbleached, soda poplar, soda straw, sulphate Norwegian pine, and ground spruce. Wood pulps produced from the same wood by the same process but by different manufacturers will doubtless differ and bear the imprint of the particular procedure used in preparing the pulp. The concentration of the solutions employed, the duration of the treatment, and the subsequent bleaching are among the factors which cause the difference. In addition, the species of wood and its age affect the resulting product. The pulps selected were commercial products of repute and typical of their class.

(a) *Methods of Drying.*—In order to have a common basis of comparison, all samples were dried before being used, and all results are expressed on the basis of the dry pulps.

Summaries of various methods which have been proposed for the drying of pulps are described by Renker¹ and König and Hühn.² For the purposes of this work drying was conducted at 105°, to constant weight, under reduced pressure in the presence of phosphorus pentoxide, except in the case of ground wood. The samples were contained in tubes fitted at each end with ground-glass stoppers, which could be immediately put in place when the tube was removed from the drying apparatus. The latter consisted of a glass tube closed at one end, connected by a ground-glass joint to a bulb containing phosphorus pentoxide, and fitted with a stopcock for evacuation. The ground wood pulp, which is susceptible to decomposition at 105°, was dried over phosphorus pentoxide in a vacuum desiccator to constant weight at room temperature, according to the procedure of Renker. These methods insured the removal of moisture under conditions which minimize the danger of decomposition by oxidation. The usual practice in work of this character is to determine the moisture in a separate sample, but the method described proved more convenient. Experiments were carried out to determine whether the drying had any effect on the cellulose constants, but none was observed greater than the experimental error.

When all traces of moisture are removed from pulps, they are very hygroscopic, as is well known. The dried samples were therefore weighed in glass-stoppered weighing bottles.

III. CHEMICAL CHARACTERISTICS

A. METHODS OF ANALYSIS

The following methods of analysis are described in the literature, but the procedures employed at the Bureau differ somewhat from those of the original methods, and therefore are described in detail.

(a) *Ash*.—The ash was determined by ignition of a 1-gram sample at the lowest possible temperature.

(b) *Methoxyl*.—For the methoxyl test the familiar method of Zeisel was used in one of the many modifications of the original apparatus. The method consists in heating a weighed amount of the substance with hydriodic acid (sp. gr. 1.7) in a current of carbon dioxide. The methyl iodide which is evolved is passed through an alcoholic solution of silver nitrate, which decomposes

¹ Bestimmungsmethoden der Zellulose, Berlin; 1910.

² Bestimmung der Zellulose in Holzarten und Gespinstfasern, Berlin; 1912.

the alkyl iodide with the formation of silver iodide, which is filtered out and weighed. This determination is of value as a measure of residual lignin. König and Hühn express it as the methyl number; i. e., the amount of CH_3 contained in 1000 g of the material. The present results represent the percentage of CH_3O in the sample.

(c) *Furfural*.—The production of furfural is generally referred to pentosans, but the constitution of these as they exist in woods and cereals is obscure. In part they are hydrolyzed by bases and in part by acids, but even after these operations and removal of the lignin there is a residue which still yields furfural when distilled with acid. According to Cross and Bevan, the furfural of the residue, as also of that obtained from purified cotton, is due to furfuroids which are fermentable and hence different from the pentosans. The furfuroids do not respond to color tests typical of pentosans. The yield of furfural by distillation with hydrochloric acid (sp. gr. 1.06) and subsequent precipitation by phloroglucinol was determined substantially according to Flint and Tollens,³ observing all the precautions noted by Kröber,⁴ who has thoroughly studied the phloroglucinol method. The precipitated phloroglucides were extracted with 95 per cent alcohol to remove the methyl-furfural phloroglucide according to the method originated by Ellett and Tollens.⁵

The method as employed is as follows: The weight of sample taken was such as to yield an amount of furfural phloroglucide approximately equal to 0.2 g. One hundred cubic centimeters of hydrochloric acid (sp. gr. 1.06) was added to the sample in the distilling flask of 250–350 cc capacity. Distillation was conducted in a glass apparatus in a bath of Rose metal; and as each 30 cc of the distillate was collected, an additional 30 cc of hydrochloric acid was added through a separatory funnel. Each 30 cc of the distillate was transferred to a 600 cc beaker containing an amount of phloroglucinol dissolved in hydrochloric acid (sp. gr. 1.06) equal to twice the weight of furfural anticipated. The end of the distillation may be determined by means of filter paper moistened with aniline acetate solution, slightly acidified with acetic acid, which gives a red coloration with furfural. Tollen's reagent,⁶ orcinol in hydrochloric acid, with the addition of 20–30 drops of 10 per cent ferric chloride, is also useful as an end-point

³ Landw. Vers.-Stat., 42, p. 381; 1893.

⁴ Journ. Landwirth., 48, p. 357; 1901.

⁵ Journ. Landwirth., 53(1), p. 13; 1905.

⁶ Ann., 260, p. 395; 1890.

detector. The distillate is made up to 400 cc by adding the necessary amount of hydrochloric acid (sp. gr. 1.06) well stirred, and allowed to stand 18 hours. During this time the precipitated phloroglucide changes from a gray slime to a sandy powder which admits of filtration. The precipitated phloroglucide was collected on a Munroe platinum Gooch crucible and washed with 150 cc of distilled water at room temperature. Crucible and contents were dried for exactly four hours in an air bath at 100° according to the recommendations of Kröber, and transferred while still hot to a weighed glass-stoppered weighing bottle of convenient capacity. Kröber has shown the necessity of transferring the crucible while still hot because of the extreme hygroscopicity of the phloroglucide.

The method of Ellett and Tollens for the removal of the alcohol-soluble phloroglucide, as recommended by Haywood,⁷ was employed as follows: "Place the crucible and precipitate in a 100 cc beaker, and pour into the Gooch 30 cc of 95 per cent alcohol heated to 60°. Place the beaker for 10 minutes in a water bath heated to 60°. Remove beaker and crucible and draw off the alcohol by suction. Repeat the alternate extraction and suction from three to five times, according to the color of the filtrate obtained. After the final extraction place the crucible in an oven and again dry at 100° for four hours, and weigh in a glass-stoppered weighing bottle."

Two corrections are applied to the final result—one for solubility in 400 cc of hydrochloric acid and 150 cc of wash-water, the other for solubility in 95 per cent alcohol at 60°. The solubility in acid and wash-water, as determined by Kröber, amounts to 0.0052 g. Haywood found the average solubility in 95 per cent alcohol to be 0.0037 g. These corrections are incorporated in the conversion tables of Kröber and of Ellett and Tollens. They have been applied to all results.

The alcohol-soluble product consists of methyl-furfural phloroglucide. Votacek⁸ states that methyl furfural from rhamnosans and fucosans reacts with phloroglucinol to form a cinnabar-red condensation product which slowly changes to a reddish brown. When hydrochloric acid is removed from the precipitate it assumes an ocher-yellow color. It is soluble in alkali and alcohol.⁹

In all determinations of furfural the alcohol-soluble portion has had the same color as the furfural phloroglucide. According to

⁷ Bull. 116, Bureau of Chemistry, p. 63.

⁸ Ber., 30, p. 1195; 1897.

⁹ Ellett and Tollens, Ber., 38, p. 493; 1905. Widtsoe and Tollens, Ber., 33, p. 140; 1900.

Widtsoe and Tollens¹⁰ the presence of considerable amounts of furfural darkens the color of the precipitate and the red methyl-furfural phloroglucide is masked. Erdmann and Schaefer¹¹ obtained hydroxymethyl furfural among the products of the dry distillation of cellulose. Düll¹² noted that hydroxymethyl furfural obtained by the action of oxalic acid on levulose under increased pressure was decomposed to levulinic acid when the action of the oxalic acid was prolonged or when the hydroxymethyl furfural was heated with dilute sulphuric acid. Theoretically the presence of traces of hydroxymethyl furfural or its decomposition product is possible in the phloroglucide precipitate, but has not been proven.

G. S. Tilley, formerly of this Bureau, employed the furfural method and suggested the use of constant-boiling hydrochloric acid as a condensing agent rather than acid of specific gravity 1.06. Distillation with the latter is accompanied by a constant change in the strength of the acid, the distillates becoming increasingly stronger. In order to determine the influence of the two media upon the condensation, a distillation was carried out with each acid. With the constant-boiling acid the distillation is more rapid, but the results obtained were substantially alike.

(d) *Copper Number.*—The copper number is determined by heating about 3 g. of cellulose with water and Fehling's solution. One hundred times the ratio of the weight of the copper in the precipitated copper suboxide to the weight of dry cellulose is called the copper number. It is a measure of the free carbonyl groups and hence of stability, for the celluloses of maximum resistance contain few free carbonyl groups. The method which has been developed by Schwalbe¹³ and his pupils involves the use of special apparatus fitted with a stirring device. The present values have been obtained, according to the method of Schwalbe, in a round-bottom flask of 1-liter capacity heated over a water bath and without the mechanical stirrer.

Two to three grams of dry pulp was transferred to the flask and 100 cc of water added. The flask and contents were brought to the temperature of the water bath, and when the maximum temperature was attained 100 cc of Fehling solution was added. The sample remained in contact with the Fehling solution for exactly 15 minutes. At the expiration of this period 1 g of kiesel-

¹⁰ Ber., 33, p. 144; 1900.

¹¹ Ber., 43, p. 2398; 1910.

¹² Chem. Zeit., 19, p. 216; 1895.

¹³ Schwalbe, *Chemie der Zellulose*, Berlin, 1911; Schulz, *Zur Kenntnis der Zellulosearten*, Berlin, 1911.

guhr, purified according to Schulz,¹⁴ suspended in 100 cc of water, was added to the contents of the flask, which were filtered through a Büchner funnel as rapidly as possible. Two sheets of S. & S. 590 paper formed a convenient filtering medium. The residue was washed with hot water until the acidified filtrate no longer reacted with potassium ferrocyanide. It was then transferred to a casserole, treated first with hot 5 per cent nitric acid (sp. gr. 1.027) and washed, and then treated with hot 5 per cent ammonia (sp. gr. 0.979). The acid and alkaline solutions were filtered and evaporated in separate casseroles or lipped crucibles of convenient size; the residues were ignited to remove organic matter, taken up with 2 per cent nitric acid (sp. gr. 1.0106), filtered; and the copper determined in the combined filtrates by electrolysis.

Inasmuch as an amount of cupric copper, definite for any particular cellulose, is retained by the cellulose in addition to the cuprous oxide, a correction must be applied. This correction, of the nature of a blank, Schwalbe has called the "cellulose number." In the present work this cellulose number has been determined according to Schwalbe, but without his special apparatus. Although the procedure differs from that proposed by Schwalbe in respect to apparatus, it furnishes reproducible results. The sample remained in contact with 100 cc of water and 100 cc of Fehling solution in a liter flask at room temperature for 45 minutes. It was washed with 500 cc cold water to remove excess Fehling solution, then with hot water. In other respects the procedure follows that already outlined for the copper number. It is assumed that at room temperature no reduction takes place in the fiber and none has been observed.

(e) *Cellulose*.—The percentage of cellulose present in the pulp was determined according to the chlorination method of Cross and Bevan, with slight modifications. The method depends upon chlorination of the lignin complex and removal of the chlorinated product from the cellulose by means of dilute sodium-sulphite solution, in which it is soluble.

The method of Cross and Bevan was employed as follows: Approximately 1 g of the dry pulp was placed in a flask and saturated with water in an apparatus constructed entirely of glass. Chlorine was generated by the action of concentrated hydrochloric

¹⁴ Kieselguhr, previously calcined, is digested with Fehling solution for one hour and then filtered and washed with distilled water. A portion is tested to determine whether it exerts any reducing action. If satisfactory, it is digested with concentrated nitric acid for several hours and washed until no more copper is present when tested with potassium ferrocyanide. It is then digested a short time with hydrochloric acid and thoroughly washed with distilled water. A weight of 20 grams is used suspended in 1 liter of distilled water.

acid upon potassium permanganate and the chlorine washed by passing through distilled water. The flask containing the sample was surrounded by ice and was allowed to remain in contact with the chlorine gas for one hour. After removing the chlorine from the flask by an aspirator, the pulp was washed with distilled water and with three successive portions of 1 per cent sodium-sulphite solution at steam-bath temperature. Each portion of the solution remained in contact with the pulp for exactly three minutes and was then poured into a beaker. The pulp was washed with hot distilled water. Detached fibers carried into the solutions and wash water were allowed to settle, the supernatant solution poured away, and the residue filtered. The major portion of the sample was then added to the filter. The Gooch-Munroe crucible and contents were dried in a vacuum apparatus, similar to that described above for pulp drying, and weighed. After ignition the residual ash was weighed. The results therefore are based on dried, ash-free samples.

A little experience with the chlorination method indicates the necessity of adhering rigidly to a definite procedure, if reproducible results are to be obtained. Prolonged treatment with the sodium sulphite solution at water-bath temperature attacks the residual cellulose. Under this treatment ground-wood pulps appear to lose more than other pulps. Renker has studied the more important methods which have been proposed for the determination of cellulose and has concluded that the chlorination method furnishes the highest and most reproducible results of any. Objection has been made to the method because there is but little action on the furfural-yielding complex, which remains in the residual cellulose. The method for pulps recently suggested by Johnsen¹⁵ provides for the removal of the complex by acid hydrolysis. The fibers are treated with a mixture of glycerol and acetic acid and heated at 135° for two hours. After washing with hot water they are transferred to a small bottle and shaken with a mixture of sodium nitrate and sulphuric acid for half an hour. After neutralizing with alkali the material is digested over a water bath, removed to a crucible with perforated disk, washed, dried, and weighed.

(f) *Gain on Nitration.*—In order to determine the effect of nitration upon the pulps, an empirical procedure was used which furnished reproducible and comparable results. Dried samples,

¹⁵ *Pulp and Paper Magazine of Canada*, 13, p. 603; 1915.

weighing approximately 1 gram, were treated with 200 cc of a mixture of concentrated sulphuric acid and fuming nitric acid (sp. gr. 1.5) for 24 hours. The mixed acids were at 0° when added to the pulp and left at room temperature. Some picric acid was formed in the nitration of ground wood. The nitrating mixture was decanted from the pulp, which was thoroughly washed, first with distilled water at 0°, then with water at room temperature, until the washings no longer reacted acid. The nitrated pulp was transferred to a Gooch-Munroe crucible and dried at room temperature under reduced pressure over phosphorus pentoxide to constant weight and weighed in a glass-stoppered weighing bottle.

2. RESULTS OF TESTS

The following table (Table 1) shows the characteristics of the pulps used, as determined by the methods described in the preceding sections:

TABLE 1.
Chemical Characteristics of Pulps

| | Rag | Bleached sulphite spruce | Un-bleached sulphite spruce | Bleached soda poplar | Sulphate (Norwegian pine) | Bleached straw | Ground wood |
|-----------------------------------|----------------|--------------------------|-----------------------------|----------------------|---------------------------|----------------|----------------|
| Ash (per cent)..... | 0.09 .09 | 0.28 .28 | 1.14 1.12 | 0.86 .87 | 0.71 .71 | 1.32 1.32 | 1.09 1.09 |
| Methoxyl (per cent)..... | Absent | .10 .09 | .63 .64 | .03 .04 | .32 .32 | .08 .08 | 5.10 5.11 |
| Furfural (per cent)..... | .28 .33 | 2.40 2.38 | 2.81 2.79 | 11.09 11.17 | 6.45 6.41 | 18.72 18.67 | 6.21 6.31 |
| Methyl furfural (per cent)..... | .18 .12 | .38 .36 | .33 .38 | .54 .50 | .33 .25 | .45 .55 | .60 .64 |
| Copper number..... | .64 .66 | 2.98 2.83 | 1.96 1.97 | 3.13 3.25 | .60 .61 | 2.22 2.14 | 2.56 2.70 |
| Blank ^a | .34 .32 | .26 .27 | .39 .42 | .40 .47 | .34 .37 | 1.10 1.04 | .64 .69 |
| Corrected..... | .30 .34 | 2.72 2.56 | 1.57 1.55 | 2.73 2.78 | .26 .24 | 1.12 1.10 | 1.92 2.01 |
| Cellulose (per cent)..... | 99.88 99.94 | 99.24 99.19 | 95.65 95.52 | 98.50 98.58 | 98.00 98.03 | 96.30 96.10 | 66.03 66.25 |
| Gain on nitration (per cent)..... | 77.5 77.3 | 73.5 72.9 | 59.8 59.6 | 48.7 48.5 | 34.1 34.3 | 28.5 28.3 | 11.3 10.9 |

^a Called the "cellulose number" by Schwalbe.

The differences between the several pulps are indicated in the table and confirm the general conclusions already known. It is apparent that the alkaline processes of preparing pulps do not remove the furfural-yielding complex to the same extent as the acid-sulphite process. The amount of methoxyl and the per-

centage of cellulose show that bleaching removes the greater part of the residual lignin from unbleached sulphite pulp. The low copper number obtained with the sulphate pulp is of interest. A marked difference is observed in the increase in weight when the pulps are nitrated. Whether the results are caused by soluble derivatives or are due to molecular complexity is not apparent.

IV. SUSCEPTIBILITY TESTS

Inasmuch as paper pulps vary in their resistance to oxidation and hydrolysis, an attempt has been made to ascertain their relative susceptibility. The exact cause of the variation is unknown. It is generally conceded that paper prepared from good rags possesses better wearing qualities than that prepared from wood pulps. In part it is probably a result of the process used in preparing the pulp, as is evidenced by the difference in the product obtained when wood is cooked with caustic soda alone and when cooked with caustic soda mixed with sodium sulphate. It also may be a result of some inherent difference in the original materials.

The loss in weight was determined after treatment with hot water, 1 per cent caustic soda, 1 per cent sodium carbonate, and 3 per cent hydrogen peroxide for one hour and a 5 per cent solution of nitric acid for five hours. Approximately 1 g portions of the pulp were treated on a steam bath in Erlenmeyer flasks with 500 cc of each solution. The conditions employed were reproduced as carefully as possible in all tests. Before being placed in contact with the sample the reagent was brought to constant temperature over a water bath. It was allowed to act on the pulp for the exact time indicated, with occasional agitation. The reagent was then removed from the sample, which was washed with cold and then with hot distilled water until absence of the reagent was assured by a suitable indicator. Any loose fibers were allowed to settle and were washed by decantation. The residue was dried at 105° and weighed in the manner previously described. In order to obtain concordant and reproducible results, the details of the procedure must be carefully observed.

The results in Table 2 have a significance only if the pulps produced by a particular process are sufficiently alike. There is considerable variation in the behavior of the pulps toward the several reagents. In several of the tests differences in the behavior of rag and wood pulps are quite marked. Sulphate pulp appears to lose more through oxidation than through hydrolysis.

TABLE 2
Susceptibility Tests, Showing Percentage Loss in Weight

| Samples | Hot water, 1 hour | 1 per cent NaOH, 1 hour | 1 per cent Na ₂ CO ₃ , 1 hour | 3 per cent H ₂ O ₂ , 1 hour | 5 per cent NH ₄ NO ₃ , 5 hours |
|-------------------------------|----------------------|-------------------------------|---|---|--|
| Rag..... | 0.05 .07 | 1.06 1.04 | 0.22 .28 | 0.3 .4 | 3.00 2.82 |
| Bleached sulphite spruce..... | 1.22 1.27 | 9.23 9.28 | 4.92 4.82 | 2.4 2.6 | 6.34 6.44 |
| Bleached soda poplar..... | 2.04 2.06 | 11.21 11.10 | 5.17 5.22 | 3.5 3.7 | 11.24 11.42 |
| Sulphate..... | 1.46 1.43 | 3.07 2.14 | 1.63 1.66 | 8.7 8.9 | 12.0 12.5 |
| Bleached straw..... | 3.91 3.96 | 10.14 10.25 | 6.47 6.50 | 9.1 9.3 | 21.1 21.4 |
| Ground wood..... | 3.3 3.7 | 13.6 13.8 | 8.2 8.3 | 13.1 12.2 | 57.0 55.0 |

V. DETERIORATION OF GROUND WOOD PULP

Although paper prepared from ground wood is not expected to possess the permanence of that produced from pure celluloses, it seemed desirable to make a short study of the chemical changes produced in such pulp during disintegration as measured by the changes in the chemical characteristics of cellulose. Although numerous factors, including temperature, moisture, sunlight, active oxygen, residual acid, chlorine, and salts, the presence of resins, and the possible action of sizing agents may exert a destructive influence upon paper, the study was confined to the action of but three of these—light, temperature, and ozonized air in the presence of air and moisture. The ground spruce wood used in the previous work was employed. The pulp was disintegrated in a small beater, and handmade sheets were prepared of as uniform thickness as possible, about 0.003 inch.

In addition to the determination of chemical characteristics which have already been described, the acid number was determined, in terms of the milligrams of caustic soda neutralized by 1 g of pulp. Tenth normal solutions of caustic soda and hydrochloric acid were used. Dry samples, in Erlenmeyer flasks, were treated with a slight excess of the alkali, which was previously determined on a separate sample. The samples were heated to incipient boiling and immediately titrated back with acid, using phenolphthalein as indicator.

(a) *Sunlight*.—Each side of the sample was exposed to sunlight for 75 hours. The samples were so arranged between glass plates that they were always moist and that air had free access. Since

the glass excluded ultra-violet rays, the effect of these does not influence the results. The samples were discolored after a few hours and finally became dark yellow. This color was found to be superficial, and the exposed sheet when split apart retained the appearance of the original sample. After 75 hours the reaction as determined by the color was assumed to be complete.

(b) *Ozonized Air*.—Another series of samples in sheet form was subjected, in a glass tube in diffused light, to the action of a stream of air containing ozone. The ozone was generated by the action of 10 g of chlorine-free sodium persulphate upon 250 cc of concentrated sulphuric acid, a stream of air being passed through the mixture. The latter was renewed when necessary. A stream of air saturated with water vapor entered the glass tube in conjunction with the active oxygen. No attempt was made to secure a quantitative stream of ozone, since it was intended that the action should be continued until the maximum effect was produced and the pulp disintegrated. A marked darkening of the color of the pulp was observed after six hours. The sample became reddish brown and finally acquired the dark coffee color characteristic of old newspapers. After 25 hours a pungent odor resembling volatile organic acids, notably acetic, was noticed in the tube. At the end of 60 hours the pulp was extremely friable and readily fell apart between the fingers. The reaction was assumed to be complete for all practical purposes.

(c) *Temperature*.—A third series of samples was heated in an air bath for 20 hours with temperature control at 100° and a fourth series at 150° for the same period. The higher temperature caused a marked darkening of the pulp.

TABLE 3
Effect of Deterioration on Ground Wood Pulp

| | Original pulp | Sunlight | Ozonized air | 100°, 20 hours | 150°, 20 hours |
|---------------------------------|---------------|--------------|--------------|----------------|----------------|
| Methoxyl (per cent)..... | 5.10 5.11 | 4.60 4.59 | 4.73 4.74 | 4.77 4.73 | 4.50 4.46 |
| Furfural (per cent)..... | 6.24 6.21 | 5.40 5.42 | 5.87 5.77 | 5.75 5.69 | 4.68 4.60 |
| Methyl furfural (per cent)..... | .60 .64 | 1.06 1.01 | .85 .96 | .95 1.05 | 1.12 1.08 |
| Copper number..... | 2.5 2.7 | 9.0 9.1 | 11.8 12.0 | 4.0 4.1 | 13.5 13.7 |
| Blank..... | .6 | 1.5 | 1.0 | 1.1 | 1.7 |
| Copper number corrected..... | 1.9 2.0 | 7.5 7.6 | 10.8 11.0 | 2.9 3.0 | 11.8 12.0 |
| Acid number..... | 16.3 15.8 | 50.0 52.0 | 63.0 63.4 | 26.4 27.5 | 63.0 |

The direction of the changes taking place in ground wood pulp subjected to sunlight, ozonized air, and increased temperature is alike in all cases, but differs somewhat in degree. The amounts of furfural and methoxyl are decreased and there is a marked increase in the copper number. There is an increase in the amount of methyl furfural in connection with the decreased yield of methoxyl. There is also an increase in the amount of caustic soda neutralized by the pulp. Evidently the process of disintegration, which is accompanied by a loosening of the carbonyl bonds, is also accompanied by oxidation to acid, some of which may have been volatilized. These changes are not accompanied by proportionate changes in the strength of the pulp; e. g., the effects of sunlight and of active oxygen upon the chemical constants appear very similar. In reality the pulp treated by active oxygen fell apart between the fingers, whereas sunlight had but slight effect upon the strength of the pulp as determined by the "pop test" in a Mullen tester.

VI. SUMMARY

Samples of paper pulps, each representing a different method of preparation and with one exception of American manufacture, have been examined to determine their chemical properties. The loss in weight produced by reagents causing hydrolysis and oxidation and the gain in weight when nitrated have been determined with the same pulps. The effect of sunlight, temperature, and ozonized air on the chemical constants of ground wood has been ascertained.

WASHINGTON, October 27, 1916.

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